

LACTOPRENE EV ELASTOMER

Effect of Plasticizers

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The properties of Lactoprene EV vulcanizates compounded with a number of plasticizers were studied to find plasticized elastomers having relatively low brittle points in addition to the desirable characteristics of unplasticized Lactoprene EV.

THE preparation and certain properties of Lactoprene EV (copolymer of 95% ethyl acrylate and 5% 2-chloroethyl vinyl ether) and its vulcanizates were described in recent papers (7, 16). Although the vulcanizates have exceptional flex life and resistance to high temperature, oils, oxidation, and sunlight, the relatively high brittle point (about -15°C . or 5°F .) is objectional for some applications. In view of the several outstanding properties of Lactoprene EV and the paucity of information on this type of elastomer, the investigation of acrylic vulcanizates was extended to include plasticized EV compositions. The purpose of this study was to find plasticized elastomers having relatively low brittle points in addition to the desirable characteristics of the unplasticized material and to improve resilience, water resistance, and other rubberlike characteristics.

METHODS AND MATERIALS

The samples were compounded by the master batch technique previously described (7). The following standard recipe was used in most experiments.

Brittle points, determined by the method of Selker, Winspear, and Kemp (21) were used as a screening test, although brittleness

tests and flexibility tests are no longer recognized as adequate for complete evaluation of low temperature properties. The cooling medium used was a mixture of low boiling paraffins; tests were made after the specimen had been immersed for 2 minutes. Resilience measurements were made with a Bashore resiliometer; pieces of the standard test slab ($6 \times 6 \times 0.075$ inch) were grouped so that the total thickness was 0.5 inch. Since this instrument is designed for measuring rebound at small deformations, the data would not be expected to correlate with those of the Goodyear-Healy rebound resiliometer. Swelling tests were run by American Society for Testing Materials, Method B, Designation D 471-43T. Heat resistance was determined by suspending specimens in a mechanical convection oven at 300°F . for 3 days, followed by examination of the aged specimens at room temperature; other tests were according to A.S.T.M. specification D 412-41.

STANDARD RECIPE

	Parts by weight
Lactoprene EV	100
Stearic acid	1
Tetramethylthiuram monosulfide	1
Trimene base	1
Sulfur	2
SRF black	50
Plasticizer	10

Some variety in chemical structure of the plasticizers (Table I) was obtained by employing phosphates, sebacates, a fat acid ester, a polyether formal, various ether-esters, a sulfonamide, chlorinated diphenyl, a phthalate, silicon derivatives, and a carbonate. Plasticizers known to be efficient in lowering the brittle point of other elastomers and resins were used in most instances.

TABLE I. PLASTICIZERS

Plasticizer No.	Chemical Name	Trade Name	Manufacturer's Symbol	Type
1	Tributoxyethyl phosphate	KP-140	KP-140	Phosphate
2	Tri-2-ethyl hexyl phosphate	Flexol TOF	TOF	Phosphate
3	Di-2-ethyl hexyl sebacate	...	DOS	Sebacate
4	2-Butoxyethyl stearate	Butyl Cellosolve stearate	BCS	Ether-ester
5	Triglycol dioctylate	Plasticizer SC	SC	Ether-ester
6	Triglycol dihexoate	Flexol 3GH	3GH	Ether-ester
7	Polyethylene glycol di-2-ethyl hexoate	Flexol 4GO	4GO	Ether-ester
8	Di-2-ethylbutyl Cellosolve succinate	Flexol CS24	CS24	Ether-ester
9	...	Thiokol TP-90B	TP-90B	Polyether formal
10	...	Thiokol TP-95	TP-95	Ether-ester
11	...	Flexol 8N8	8N8	...
12	Butoxyethyl diglycol carbonate	...	BGC	Carbonate (ether-ester)
13	2-Ethyl hexyl phthalate	Flexol DOP	DOP	Aromatic ester
14	Butoxyethyl sebacate	Monoplex 7	M7	Ether-ester
15	...	Monoplex 16	M16	Nitrile
16	n-Ethyl toluenesulfonamide	Santicizer 8	S8	Sulfonamide
17	Organo-silicon oxide polymer	Dow-Corning 500	DC500	Silicone
18	Chlorinated diphenyl	Aroclor 1254	A1254	Chlorinated aromatics
19	...	Sylon RD-602	RD-602	Amino silane
20	...	Sylon RD-611	RD-611	Amino silane

TABLE II. PHYSICAL PROPERTIES OF PLASTICIZERS

No.	Symbol	Molecular Weight	Boiling Point ° C. Mm. Hg	Oxygen, % ^a	Viscosity, Cp. at 20° C.	Specific Gravity, 20° C.	Solubility in Water at 20° C., %
1	KP-140	398	200-232	4	28.2	1.020	0.1b
2	TOF	434.6	220	5	14.9	0.9262	0.01
3	DOS	426	256	5	15.1	0.910	0.20
4	BCS	384	215-45	4	12.5	0.855	0.0
5	SC	420	254	6	23.0	0.967	0.033
6	3GH	346	202	5	27.8	0.9946	0.02
7	4GO	446	215-90	5	25.1	0.9892	0.01
8	CS24	394	219	5	24.4	0.9856	0.01
9	TP-90B	...	200	4	29.0	0.968	0.31
10	TP-95	...	350	4	27.0	1.020	0.065
11	8N8	...	255	5	3.7	0.958	0.01
12	BGC	394.5	215	4	36.8	1.065	0.04b
13	DOP	390.5	229	5	16.4	0.986	Insol.
14	M7	402.6	227	2	23.84	1.53b	...
15	M16	...	251	6	...	0.900b	...
16	S8	199.3	750	1.190b	0.13 (123°)
17	DC500	...	120-160	0.5	...	0.918b	Insol.
18	A1254	...	365-390	760	...	1.54b	...
19	RD602	...	83	20	...	0.926	...
20	RD611	3.25b	0.931	...

^a Calculated or obtained from the manufacturer.^b At 25° C.

Physical properties (Table II) were obtained from the manufacturer and literature (4, 19) or determined experimentally.

Four copolymers prepared on a small pilot plant scale were used in this investigation.

PROPERTIES OF PLASTICIZED COMPOSITIONS

Of the 20 plasticizers shown in Table I, 10 produced a substantial lowering of the brittle point. These were, in approximate order of decreasing effectiveness: Thiokol TP-90B, Thiokol TP-95, Flexol 4GO, Monoplex 7, butoxyethyl diglycol carbonate, Flexol 3GH, Flexol CS24, Flexol DOP, Monoplex 16, and Santicizer 8. The brittle point was lowered from -13° C. to between -29° C. and -35° C. when 10 parts (approximately 6.1%) of the plasticizers were used with the base recipe (Table IV). Since Sylon RD-602 and Sylon RD-611 reacted during the vulcanization and some of the butyl Cellosolve stearate exuded, their plasticizing effects were impaired. Tensile strength was lowered somewhat by the plasticizers, but the plasticized compositions

were strong enough for many uses. Several of the plasticized compositions had tensile products higher than that of the control. Some variations were noted in elongation, modulus, hardness, break set, and rebound as the result of using plasticizers (Table IV). In general the plasticized compositions had lower modulus and higher elongation values than the control. The compositions containing Sylon RD-602 and Dow-Corning 500 had lower elongations than that of the control.

Apparently there is a relation between brittle point and resilience for most of the plasticized compositions (Figure 1). A similar relation has been reported for butadiene copolymers (2).

The plasticizers (Table II) had high boiling points, and hence it is likely that they would be lost from the plasticized compositions at a low rate at room and moderate temperatures. The standard aging test of 3 days at 300° F. in a mechanical convection oven was so severe, however, that a considerable portion of the plasticizers was lost. Volatilization of moisture and vulcanizing ingredients were responsible for some of the decrease in weight of the specimens. The average loss for a series of plasticized samples (Table IV, 10 parts plasticizer used with the base recipe) during the test was 7.25%, whereas the unplasticized control lost 3.5%. This loss, corresponding to over 60% of the plasticizer initially present, was accompanied by decrease in resilience. Although the loss in weight of the vulcanizates probably was roughly proportional to the volatility of the plasticizer present, it is known (11) that factors other than volatility affect retention of plasticizer.

Thiokol TP-90B was chosen for further study, increased amounts of both plasticizer and carbon black being used. Results obtained with 15 and 20 parts of plasticizer added to the base recipe as well as with the addition of 10 and 25 parts of channel black are shown in Table V.

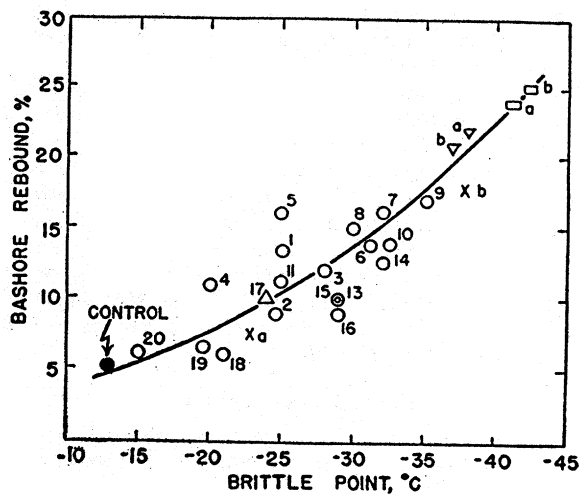


Figure 1

TABLE III. COPOLYMERS USED IN PLASTICIZER EXPERIMENTS

Copolymer No. ^a	Composition	Experiment No.
AC79E25	95% ethyl acrylate, 5% 2-chloroethyl vinyl ether	2218, 2221-3
AC79E35	95% ethyl acrylate, 5% 2-chloroethyl vinyl ether	2245, 6, 2252
AC79E30	75% ethyl acrylate, 20% n-butyl acrylate, 5% 2-chloroethyl vinyl ether	2359, 2360
G-157	95% ethyl acrylate, 5% 2-chloroethyl vinyl ether	2370-5
		2272-3
		2189

^a The first three samples were prepared by the Chemical Engineering and Development Division of this laboratory. The fourth sample was prepared by The B. F. Goodrich Company.

TABLE IV. PROPERTIES OF PLASTICIZED LACTOPRENE EV VULCANIZATES

TABLE IV. PROPERTIES OF PLASTICIZED DIACETALDEHYDE IN VARIOUS PLASTICIZERS														Oven Aged for 3 Days at 300° F.				
Spt. No.	Plasticizer ^a	Curing Time, Min. at 298° F.	Tensile Strength, Lb./Sq. In.	Modulus at 200%, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Break Set, %	Shore Resilience, %	Crescent Tear Strength, Lb./In.	Brittle Point, ° C.	Tensile strength, lb./sq. in.	Ultimate elongation, %	Shore A hardness	Break set, %	Shore Resilience, %			
2218	None	30	1600	550	500	47	10	4										
		60	1820	740	440	52	9.7	5										
		120	1910	890	420	52	10	5	120	-13	1850	240	55	6	3.5			
2221	SC	30	1400	340	580	40	14	14										
		60	1540	510	520	45	11.5	15										
		120	1650	540	530	48	12.3	16	145	-25	1770	300	52	7	4			
2222	KP-140	30	960	160	750	36	20.7	14										
		60	1240	210	750	39	16.4	14										
		120	1390	200	760	40	18.8	13.5	169	-25	1840	350	51	8	4			
2223	TOF	30	1280	270	630	40	12.9	10										
		60	1510	370	610	42	14.1	10										
		120	1550	410	530	45	11.8	9	135	-24.5	1820	290	53	5.5	3			
2224 ^b	DOS	30	1510	320	640	42	13	12										
		60	1650	510	520	43	11.9	12										
		120	1640	530	520	46	12.8	12	122	-27	1660	280	54	6	4			
2225	TP-90B	30	1530	400	570	44	11	17										
		60	1640	520	520	45	15.1	17										
		120	1720	680	480	49	14.2	17	125	-35	1980	310	55	9	5			
2226	TP-95	30	1650	500	560	45	14	15										
		60	1700	610	490	46	13.6	16										
		120	1670	610	480	49	12.7	14	129	-32.5	1880	310	55	6	4			
2227	4GO	30	1520	430	560	44	12.9	14										
		60	1660	470	550	45	16.1	15										
		120	1640	560	480	50	11.3	16	125	-32	1830	260	55	5	4			
2228 ^b	BCS	30	1480	300	680	41	18.0	11										
		60	1590	400	620	44	14.7	11										
		120	1570	420	560	45	17.2	11	129	-20	1630	290	55	5.5	4			
2245	CS24	30	1400	340	540	41	9.2	14.5										
		60	1570	440	500	45	9.7	15										
		120	1560	360	450	45	10.7	15	116	-30	1760	260	55	5	4			
2246	8N8	30	1330	330	520	40	9.3	11										
		60	1480	430	500	42	6.2	11										
		120	1420	400	490	42	7.2	11	165	-25	1700	270	53	4	4			
2252	3GH	30	1210	120	650	36	13.7	13.5										
		60	1475	230	610	41	14.4	14										
		120	1510	360	510	45	12	14	142	-31	1760	290	54	4	3.5			
2359 ^c	M16	30	1120	240	950	35	...	10										
		60	1480	340	890	39	...	10										
		120	1610	470	730	44	...	10	..	-29	1630	410	50	..	5			
2360 ^c	M7	30	980	90	870	35	...	15										
		60	1380	160	870	37	...	13.5										
		120	1600	240	750	41	...	13	..	-32	1840	370	50	..	5			
2370 ^d	DC500 (7.5) DOP (7.5)	30	1250	600	400	51	13.8	9										
		60	1270	690	370	52	11.5	10										
		120	1320	790	340	55	9.8	10	..	-24	1530	240	72	9.4	7			
2371	A1254	30	1160	120	860	35	21.3	6										
		60	1490	200	800	36	19.2	6										
		120	1790	350	670	43	19.6	6	..	-21	1880	340	49	5.7	4			
2372	DOP	30	970	20	830	34	17.5	10										
		60	1400	140	840	35	16.7	10										
		120	1570	230	720	40	16.1	10	..	-29	1910	360	50	6.9	4			
2373	88	30	1250	240	760	39	17.3	9										
		60	1480	230	710	41	17.6	9										
		120	1560	400	570	45	13.5	9	..	-29	1890	320	52	4.9	4			
2374 ^e	RD-611	30	940	300	600	50	...	6										
		60	1320	420	540	52	...	6										
		120	1480	590	460	55	...	6	..	-15	1420	330	60	..	4			
2375 ^e	RD-602	30	1200	420	550	48	...	6.5										
		60	1360	610	430	54	...	6.5										
		120	1380	860	340	55	...	6.5	..	-19.5	1500	240	66	..	6			
2189/	BGC	60 ^c	1370	290	720	51	26	4										
		120 ^c	1450	400	610	51	24	4	..	-32	1560	260	63	..	2			

^a Ten parts plasticizer used in base recipe.^b Plasticizer was incompatible.^c Two parts stearic acid.^d Two plasticizers, 7.5 parts of each; stearic acid 2; sulfur 3; and Trimene base 4 parts, used.^e Two parts Trimene base and 50 parts easy processing channel black used instead of semireinforcing.

Polymer G-157 used; since this copolymer is cured more slowly than other preparations of Lactoprene EV, 312° F. was used; the resilience of the vulcanizate was abnormally low.

Here again tensile strength, elongation, and hardness were not greatly affected by the use of additional plasticizer. The use of an additional 10 parts of channel black (Micronex) did not appreciably alter the brittle point, hardness, or resilience. The effect of 25 parts of channel black was pronounced, however, the brittle point being raised 14° C. As shown by Figure 1, the resilience also was lowered, but the relation between resilience and brittle point was maintained. According to Boyer and Spencer (3), the effect of increasing the loading is to raise the brittle point.

Moderately smooth curves (Figure 2) were obtained by plotting brittle point and resilience against parts of plasticizer in the

vulcanizates, whereas, Boyer and Spencer (3) show that straight lines result in some instances when brittle point is plotted against percentage plasticizer or when the reciprocal of the brittle point (° K.) is plotted against the square root of the weight fraction of the polymer.

The behavior of the plasticized compositions in water and in certain standard hydrocarbon fuels was studied also (Table VI). The plasticized specimens resembled unplasticized Lactoprene EV in that swelling occurred on immersion in water; equilibrium was reached only after a prolonged period. Both the nature and quantity of plasticizer influenced swelling (Table VI). One

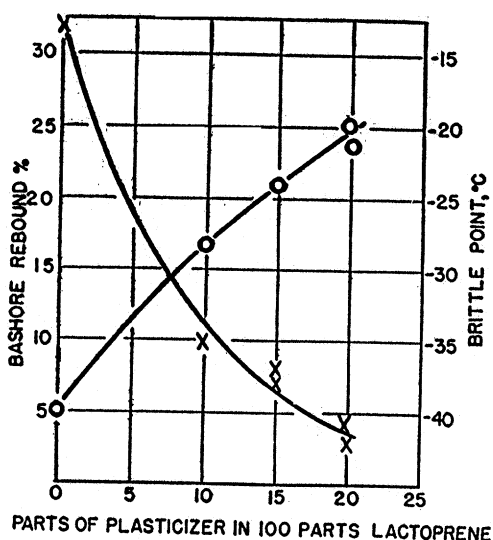


Figure 2

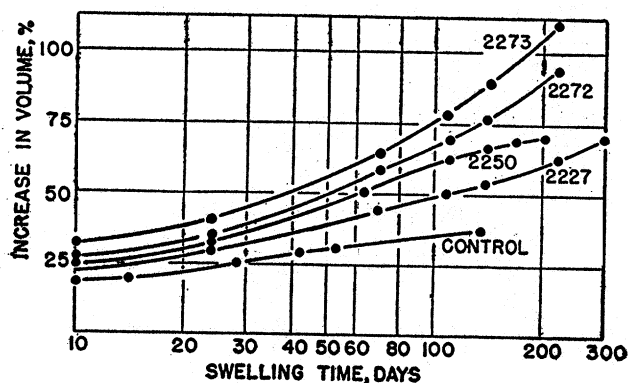


Figure 4

sample (2226, Thiokol TP-95) seemed to have reached equilibrium after swelling in water for 100 days, whereas the others continued to absorb water (Figures 3 and 4). The amino silanes improved resistance to swelling in water at room temperature.

Since swelling is influenced by state of cure, it should be noted that the vulcanizates containing the various plasticizers were not cured to constant modulus. Swelling data obtained in the present work bear a rough inverse relation to modulus, but the rela-

TABLE V. EFFECT OF INCREASED PLASTICIZER AND CARBON BLACK LOADINGS^a

Sample No.	2218	2225	2247	2248	2249 ^b	2250 ^b	2301 ^c
TP-90B, parts	0	10	15	20	15	20	20
Tensile strength, lb./sq. in.	1910	1720	1380	1410	1530	1320	1500
Elongation, %	420	480	575	570	570	570	450
Modulus, 300%	1490	1150	640	660	800	680	1070
Shore A hardness	52	49	45	41	44	41	44
Break set, %	10	14.2	13	16	17	14	14
Resilience, %	5	17	22 ^d	24	21	25	10
Crescent tear, lb./in.	129	138	171	144	..
Brittle point, °C.	-13	-35	-38	-41	-37	-42	-28
Oven aged for 3 days at 300° F.							
Tensile strength, lb./sq. in.	1850	1980	1760	1770	1820	1750	..
Elongation, %	240	310	300	300	280	280	..
Shore A hardness	55	55	53	53	59	59	..
Break set, %	6	9	6	6	5	7	..
Resilience, %	3.5	5	3	3	4	4	..
Weight loss on aging, %	3.5	..	12.2	9.9	9.5	11.7	..

^a Samples cured for 120 minutes at 298° F.

^b Ten parts channel black added to base recipe.

^c Twenty-five parts channel black added to base recipe.

^d Determined on sample cured for 60 minutes.

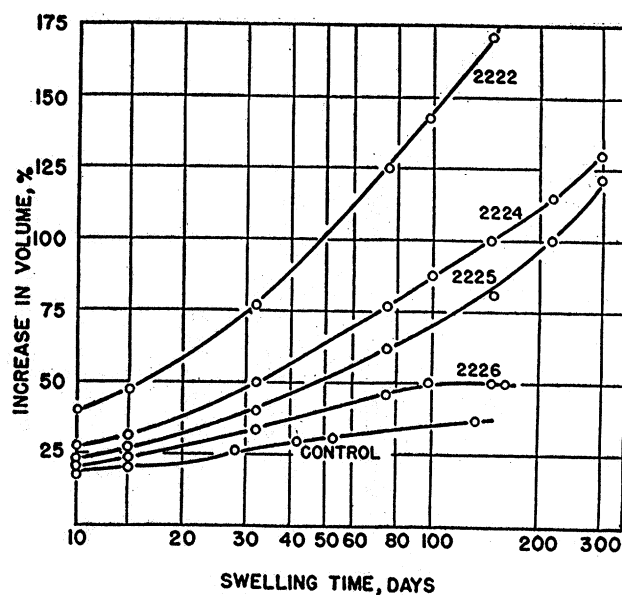


Figure 3

tion was not evaluated because most of the samples did not reach equilibrium swelling. Flory (10) demonstrated that at equilibrium the modulus of Butyl rubber swollen in cyclohexane is inversely related to the 5/3 power of the swelling ratio.

Equilibrium was reached quickly when the vulcanizates were immersed in standard hydrocarbon solvents. In toluene, for example, equilibrium was reached in about 5 hours. With SR-10, the swelling was small, and equilibrium was reached quickly. In general, the Lactoprene EV vulcanizates swelled little between 3 and 98 days in hydrocarbons. Swelling of the samples was negligible in Circo light process oil. Considerable information on the swelling of Lactoprene EV in various solvents has been published (7).

Butyl rubber and Paraplex X-100 (polyester elastomer), which may be regarded as resinous or polymeric plasticizers, also lowered the brittle point of Lactoprene EV. The decrease in brittle points of the blends, however, was accompanied by changes in

TABLE VI. SWELLING OF PLASTICIZED LACTOPRENE IN STANDARD HYDROCARBON FLUIDS AND WATER AT ROOM TEMPERATURES^a

Sample No.	Plasticizer	Increase in Volume, %			
		In SR-6, 7 weeks ^b	In SR-10, 7 weeks ^c	In water, weeks	
2218	Control	64	14	30	35
2221	SC	56	3	38	47
2222	KP-140	71	4	91	142
2223	TOF	60	6	44	68
2224	DOS	73	6	57	88
2225	TP-90B	62	3	44	70
2226	TP-95	64	4	36	50
2227	4GO	60	3	37	49
2228	BCS	60	6	50	65
2245	CS24	64	3	48	60
2246	SN8	60	3	44	64
2248	TP-90B	58	0	53	70
2249	TP-90B	82	1.5	44	57
2250	TP-90B	54	0	47	60
2252	3GH	64	1.5	45	60
2272 ^d	None	110	16	48	67
2273 ^d	TP-90B	110	11	52	75
2272	DOF	68	3	23.5	..
2360	Monoplex 7	68	4.5	27	..
2359	Monoplex 16	66	1.5	24	..
2373	Santicizer 8	64	8	22	..
2370	DOF + DC500	54	13	21	..
2371	A1254	73	6	20	..
2375	RD602	52	9	13.5	..
2374	RD611	75	9	20	..

^a Tested by A.S.T.M. Method B, Designation D 471-43T, on samples cured for 120 minutes at 298° F.

^b Equilibrium swelling in reference fuel (diisobutylene + 40% aromatics).

^c Equilibrium swelling in reference fuel (diisobutylene).

^d Copolymer: 75% ethyl acrylate, 20% n-butyl acrylate, and 5% chloroethyl vinyl ether.

TABLE VII. EFFECTS OF *n*-BUTYL AND *n*-OCTYL ACRYLATES ON BRITTLE POINT OF ETHYL ACRYLATE COPOLYMER VULCANIZATES*

Sample No.	<i>n</i> -Butyl Acrylate, %	<i>n</i> -Octyl Acrylate, %	Brittle Point, °C.
1	10	0	-18
2	20	0	-20
3	35	0	-29
4	40	0	-32
5	100	0	-50
6	0	10	-22
7	0	20	-31
8	0	30	-33
9	0	40	-35
10	0	100	-65

* Ethyl acrylate copolymers, prepared by emulsion polymerization, were vulcanized by the quinone dioxime recipe (17).

other properties. For example, Butyl rubber improved the strength but impaired the oil resistance (17). Paraplex X-100, which was less effective than Butyl rubber in lowering the brittle point, had little effect on oil resistance. The decrease in brittle point (°C.) caused by incorporation of Paraplex X-100 was as follows: 10% X-100, brittle point lowered 3°; 20%, 10°; 35%, 21°; and 60%, 29°.

INTERNAL PLASTICIZATION

It was pointed out in an earlier publication (17) that the brittle point of Lactoprene can be lowered by internal plasticization—that is, preparing copolymers having the plasticizing groups attached as side chains to the copolymer molecule. This general method of modifying the properties of polymers has been suggested or advocated by earlier workers (5). Several additional copolymers of this general type, prepared conveniently by polymerizing mixtures containing ethyl acrylate and either *n*-butyl or *n*-octyl acrylate, were studied briefly in the present work. Data obtained with some of these copolymers, given in Table VII, show that approximately 20% *n*-octyl acrylate and 40% *n*-butyl acrylate are required to lower the brittle point to -31° C.

Most attention was given to a polymer (Table VIII) prepared from a monomer mixture that contained 75% ethyl acrylate, 20% *n*-butyl acrylate, and 5% chloroethyl vinyl ether. This copolymer vulcanized satisfactorily as such and when plasticized with Thiokol TP-90B. The physical properties of the vulcanizate, roughly similar to those of the Lactoprene EV vulcanizate, reflected the effect of the *n*-butyl groups. The resilience and brittle point were higher and lower, respectively (Table VIII). The brittle point (-23° C.) of the butyl acrylate copolymer was not sufficiently low for some uses, but the plasticized copolymer, flexible at -38° C., should be suitable for many civilian applications.

The vulcanizates of the butyl acrylate copolymer (Table VIII) were similar to Lactoprene EV in having good heat resistance. It is apparent that, although *n*-butyl acrylate in the copolymer is not so efficient as liquid plasticizer, its effect is more permanent. These and earlier data (7, 16) show that vulcanized ethyl acrylate polymers are generally and inherently heat resistant.

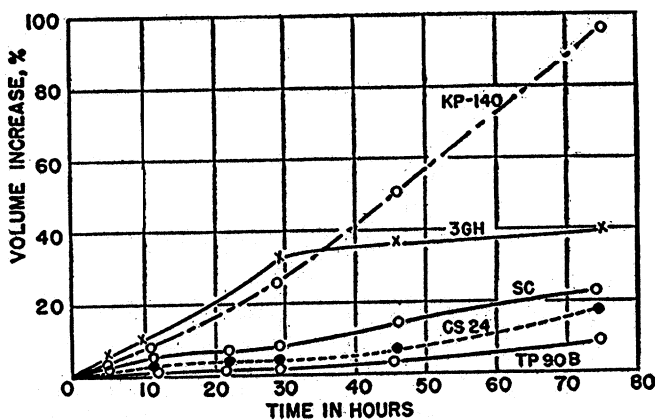


Figure 5

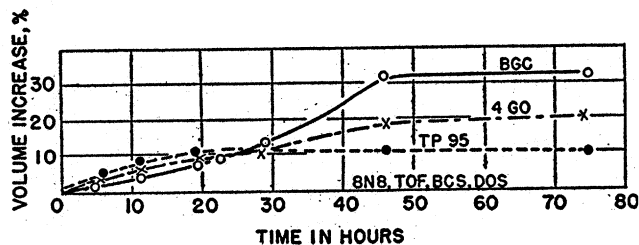


Figure 6

PLASTICIZER PROPERTIES AND ELASTOMER PERFORMANCE

Previous investigators have studied the relation between the properties and performance or efficiency of the plasticizer (1, 6, 9, 11, 14, and 20) and have listed the requirements (compatibility, permanence, thermal and chemical stability, etc.) of satisfactory plasticizers (4, 8, 13). In the present work, the relation between certain properties of the plasticizer and its suitability for use with Lactoprene EV was investigated briefly. It was anticipated from the beginning that polar groups in the plasticizer (8, 15) would enhance its compatibility for Lactoprene, which contains 32% oxygen and many ester groups.

It has been suggested (12, 13) that the solvent power of the plasticizer for the polymer is an indication of compatibility. To ascertain whether this approach would yield helpful data, uncompounded Lactoprene EV was molded, and strips of uniform size were immersed in the plasticizers. The results of these tests (Table IX and Figures 5 and 6) show that both the solvent and swelling power of the plasticizers are roughly proportional to their oxygen contents. Dioctyl sebacate, butoxyethyl stearate, Flexol TOF, and Flexol 8N8 failed to dissolve or swell Lactoprene EV appreciably. The first two of these materials are incompatible, whereas the other two are ineffective in lowering the brittle point

TABLE VIII. PROPERTIES OF BUTYL ACRYLATE COPOLYMER VULCANIZATES*

Expt. No.	Curing Time at 298° F., Min.	Tensile Strength, Lb./Sq. In.	Modulus at 400°, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Crescent Tear, Lb./In.	Break Set, %	Bashore Resilience, %	Brittle Point, °C.	Oven Aged for 3 Days at 300° F.				
										Tensile, lb./sq. in.	Ultimate elongation, %	Shore A hardness	Break set, %	Bashore resilience, %
2272 ^b	30	1015	790	590	40	192	13	7						
	60	1460	1220	530	44	139	10	7						
	120	1550	1490	420	49	116	9	7.5	-23	1510	260	51	4	5.5
2273 ^c	30	770	320	580	35	115	12	17						
	60	1130	825	590	36	135	9	19						
	120	1330	1130	470	44	108	7	18	-38	1590	290	52	6	6

* Copolymer of 75% ethyl acrylate, 20% butyl acrylate, and 5% chloroethyl vinyl ether prepared in a 10-gallon glass-lined reactor by the Chemical Engineering and Development Division of this laboratory.

^b Compounding recipe, parts by weight: copolymer 100; stearic acid 2; tetramethyl thiuram monosulfide 1; Trimene base 1; SRF black 50. For Lactoprene EV control, see Expt. 2218, Table IV.

^c Compounding recipe: Same as ^b except 10 parts Thiokol TP-90B added. For Lactoprene EV control, see Expt. 2225, Table IV.

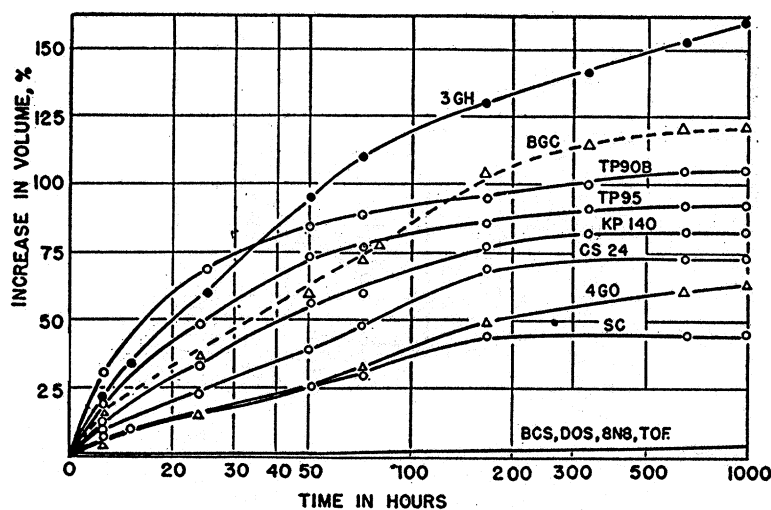


Figure 7

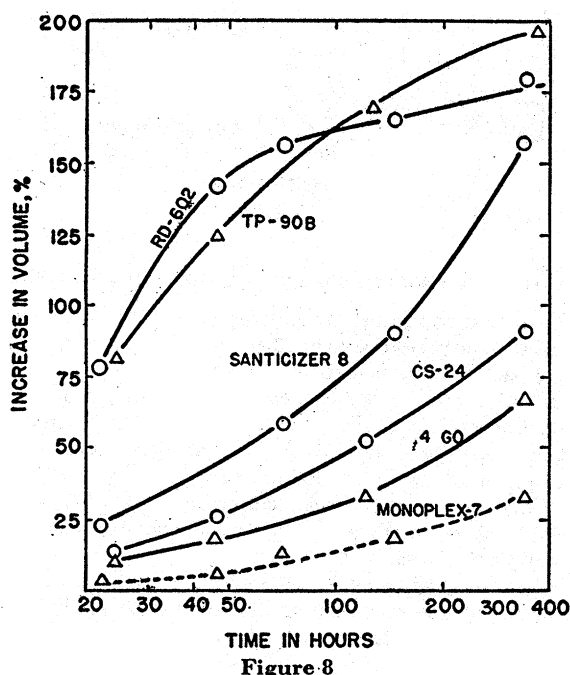


Figure 8

(Table IV). In general, the compatible and efficient plasticizers shown in Table III readily swelled or partly dissolved Lactoprene EV copolymer and had high oxygen contents, approaching that of ethyl acrylate (32%).

Jones (12) suggested that the degree of swelling of the vulcanizate in the plasticizer is useful in predicting compatibility. This method is more attractive experimentally than determining the

TABLE IX. RELATION BETWEEN OXYGEN CONTENT OF PLASTICIZERS AND THEIR SWELLING EFFECTS ON LACTOPRENE EV COPOLYMER

Plasticizer Symbol	Oxygen, %	Time Required to Swell and Partly Dissolve Copolymer, Hours
TP-90B	29.0	5
TP-95	27.0	5
3GH	27.8	12
BGC	36.8	24
KP-140	28.2	48
4GO	25.1	48
SC	23.0	48
CS24	24.4	48
DOS	15.1	..
BCS	12.5	..
TOF	14.9	..
SN8	3.7	..

action of plasticizers on the thermoplastic polymer, largely because swelling of the vulcanizate can be ascertained easily and quantitatively. Swelling data (Figures 7 and 8) obtained with Lactoprene EV vulcanizates were indeed related to certain properties of both the plasticizer and the plasticized vulcanizates in many instances. In general, the plasticizers of good swelling power had high-oxygen contents (or high oxygen + sulfur + nitrogen contents) and were efficient in lowering the brittle point. An apparent exception to this generalization is the amino silane, RD-602, which had high swelling power but was ineffective in lowering the brittle point. Probably the RD-602 was transformed into an inefficient polymeric material during vulcanization of the acrylic rubber; possibly the unmodified RD-602 would be efficient in lowering the brittle point.

Monoplex 16, a nitrile with little swelling power for Lactoprene EV (less than 1.5% after 500 hours), appeared to be compatible and moderately efficient.

The swelling power of the plasticizer might be useful in selecting compatible and useful plasticizers, but it is unlikely that swelling power alone can be used as the criterion of a satisfactory plasticizer. For example, the swelling power would be of little or no value in selecting a nonsolvent plasticizer. Butyl rubber, which presumably acts as a nonsolvent plasticizer, is effective in lowering the brittle point of acrylic elastomers (17).

ACKNOWLEDGMENT

The authors extend thanks to T. J. Fitzpatrick, 3rd, for determining brittle points and swelling data in standard solvents; T. J. Dietz and W. E. Palm, of this laboratory, for supplying the physical test data; The B. F. Goodrich Company and R. K. Eskew and W. W. Howerton, of this laboratory, for preparing lactoprene samples; and various industrial organizations for supplying the plasticizers used in this investigation.

LITERATURE CITED

- (1) Barron, H., "Modern Plastics," chap. 22, New York, John Wiley & Sons, 1946.
- (2) Borders, A. M., and Juve, R. D., *IND. ENG. CHEM.*, **38**, 1066 (1946).
- (3) Boyer, R. F., and Spencer, R. S., "Advances in Colloid Science," Vol. II, pp. 21-46, New York, Interscience Publishers, 1946.
- (4) Chicago Paint and Varnish Production Club, *Paint, Oil Chem. Rev.*, **108**, No. 21-22, 124 (Nov. 1, 1945).
- (5) Clark, F. W., *Chemistry & Industry*, **60**, 225 (1941).
- (6) DeBell, J. M., *Modern Plastics*, **20**, No. 3, 89 (1942).
- (7) Dietz, T. J., Mast, W. C., Dean, R. L., and Fisher, C. H., *IND. ENG. CHEM.*, **38**, 960 (1946).
- (8) Elam, D. W., Preusser, H. M., and Page, R. L., *Modern Plastics*, **20**, No. 9, 95 (1943).
- (9) Fligor, K. K., and Sumner, J. K., *IND. ENG. CHEM.*, **37**, 504 (1945).
- (10) Flory, P. J., *Ibid.*, **38**, 417 (1946).
- (11) Gloor, W. E., and Gilbert, C. B., *Ibid.*, **33**, 597 (1941).
- (12) Jones, H., *Trans. Inst. Rubber Ind.*, **21**, 298 (1946).
- (13) Jones, H., and Chadwick, E., *Oil Colour Trades J.*, **109**, 1044 (1946).
- (14) Jordan, O., "Technology of Solvents," chap. 6, New York, Chemical Publishing Co., 1938.
- (15) Kirkpatrick, A., *J. Applied Phys.*, **11**, 255 (1940).
- (16) Mast, W. C., Dietz, T. J., Dean, R. L., and Fisher, C. H., *Indust. Rubber World*, **116**, 355 (1947).
- (17) Mast, W. C., Rehberg, C. E., Dietz, T. J., and Fisher, C. H., *IND. ENG. CHEM.*, **36**, 1022 (1944).
- (18) Mellan, I., "Industrial Solvents," chap. III, New York, Reinhold Publishing Corp., 1939.
- (19) Morris, R. E., Hollister, J. W., and Seegman, I. P., *Rubber Age (N.Y.)*, **56**, 163 (1944).
- (20) Reed, M. C., *IND. ENG. CHEM.*, **35**, 896 (1943).
- (21) Selker, M. L., Winspear, G. G., and Kemp, A. R., *Ibid.*, **34**, 157 (1942).

RECEIVED August 6, 1948. Presented before the Division of Rubber Chemistry at the 112th Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y.